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16. ABSTRACT

As the result of screening elastomeric materials that may be suitable for formulating chemical-protective clothing, a simple test method has been developed that allows the prediction of the permeation of an organic solvent through a polymeric membrane. The test method, based on liquid-immersion absorption and desorption measurements, is simple, universal, and can be carried outr by technicians with minimal training.

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PREDICTIVE TEST METHODS—PERMEATION OF POLYMERIC MEMBRANES BY ORGANIC SOLVENTS

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INTRODUCTION

During the past four years, more than 2000 permeation tests of polymeric materials have been conducted at Southern Research Institute. These tests are generally conducted for the purpose of screening elastomeric materials that may be suitable for the formulation of chemical-protective clothing. Permeation tests are time-consuming and expensive and they often require the development of analytical methods for the permeant. These analytical methods usually are not universal, and, thus, skilled technicians may be required to conduct permeation tests.

This work[1] included the development of a simple test method that allows the prediction of the permeation of an organic solvent through a polymeric membrane. The test method, based on liquid-immersion absorption and desorption measurements, is simple, universal, and can be carried out by technicians with minimal training.

EXPERIMENTAL

For each experiment, a polymeric sample with known dimensions and weight was immersed in the solvent of interest at t=0. The sample was removed periodically from the solvent, blotted to remove excess solvent, and then weighed. It was reimmersed in the solvent after each weighing. This test was referred to as the liquid-immersion absorption test.

After the weight of the polymeric sample reached a constant value (indicating equilibrium), it was removed from the solvent and blotted to remove excess solvent. The sample was then suspended from a hook on an analytical balance, and its weight was recorded as a function of time. This test was referred to as the liquid-immersion desorption experiment. Desorption experiments were conducted only for those samples that exhibited appreciable absorption.

The materials tested were circular samples of unsupported gloves that were 3.5 cm in diameter. The identification of the gloves used is given in Table 1. The tests were conducted with the samples and solvents in the temperature range of 73 ± 6 °F.

DATA ANALYSIS

The absorption (or desorption) of a solvent by a planar sample (if edge effects are negligible) is given by:

$$M_t/M_\infty = 1 - (8/\pi^2) \sum_{m=0}^{\infty} (2m+1)^{-2} \exp(-D_0(2m+1)^2\pi^2 t/\ell^2) \quad (1)$$

where t is the time, M_t is the cumulative amount of solvent absorbed (or desorbed), M_∞ is the cumulative amount absorbed at infinite time (that is, at long times), D_0 is the diffusion coefficient for the solvent in the polymer, and ℓ is the thickness of the sample. This equation assumes that the diffusion observed is Fickian, that the swelling of the polymer sample is negligible, and that the diffusion coefficient is independent of solvent concentration in the polymer.

Absorption or desorption data may be fit to Equation 1 using nonlinear techniques to obtain an estimate of D_0 and M_∞ (the solubility, S, of the solvent in the polymer is M_∞/V where V is the volume of the unswollen sample). M_∞ is simply the maximum weight gain of the polymeric sample immersed in the solvent.

If the quantity (M_t/M_∞) is plotted as a function of $t^{1/2}/\ell$, the so-called reduced sorption curve is obtained. Fujita[2] and Crank[3] have shown that the initial slope of this curve (up to $M_t/M_\infty \approx 0.6$) may be used to estimate an apparent diffusion coefficient by using the following equation:

$$D = (\pi/16)I^2 \quad (2)$$

where D is the apparent diffusion coefficient and I is the initial slope of the reduced sorption curve. Reduced sorption curves may be plotted for absorption or desorption data. Only one of these reduced sorption curves is necessary to calculate D; however, both were used in this study when available.

Once estimates of D and S are obtained as described above, then the solvent permeation rate (J) as a function of time (through a glove sample covered on one side by an organic solvent) may be predicted using the equation:

$$J = (DS/\ell)\{1 + \sum_{m=1}^{\infty} 2\cdot\cos(m\pi)\cdot\exp(-m^2\pi^2 Dt/\ell^2)\} \quad (3)$$

The steady-state permeation rate (J_∞) may be estimated using:

$$J_\infty = DS/\ell \quad (4)$$

The breakthrough time (t_j) based on a given permeation rate (J_b) may be estimated using:

$$J_b = (DS/\ell)\{1 + \sum_{m=1}^{\infty} 2\cdot\cos(m\pi)\cdot\exp(-m^2\pi^2 Dt_j/\ell^2)\} \quad (5)$$

TEST RESULTS

Typical absorption and desorption curves are shown in Figures 1, 2, and 3. Average solubilities and diffusion coefficients determined are given for four solvents in Table 2.

PREDICTIONS

Predicted steady-state permeation rates and breakthrough times for the solvent/polymer combinations studied in this work are given in Table 3. This table also includes steady-state permeation rates and breakthrough times determined in permeation tests using the same polymeric glove samples and solvents. Figures 4 and 5 show predicted permeation-rate curves (calculated using Equation 3) and measured permeation-rate curves for acetone through nitrile rubber and acetone through natural rubber.

CONCLUSIONS

A comparison of the predicted steady-state permeation rates and breakthrough times in Table 3 with measured values for these parameters indicates that the liquid-immersion absorption and desorption test methods described here are useful for the prediction of the relative chemical-resistance of a given polymeric glove. The method would thus be useful for the screening of a large number of candidate polymeric materials by technicians with minimal training and would require relatively little capital equipment.

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W.J. Jessen and R.F. Collison (Southern Research Institute) conducted most of the work described here. The authors also acknowledge the support given by J.P. Meade (JRB Associates) and K.F. Wong and M.D. Royer (US Environmental Protection Agency) through a subcontract on EPA Contract 68-03-3113. [This manuscript does not necessarily reflect EPA policy.]

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TABLE 1. IDENTIFICATION OF GLOVE MATERIALS USED IN LIQUID-IMMERSION ABSORPTION AND DESORPTION TESTS

Glove	Manufacturer	Style No.	Nominal thickness, mil	Source
Butyl rubber	Siebe Norton, Inc. N. Charleston, SC	B-224	25	SRI stockroom
Poly(vinyl chloride)	Pioneer Industrial Products Co. Willard, OH	V-5 Quixem	5	SRI stockroom
Neoprene rubber	Edmont Coshocton, OH	29-875	19	Southern Safety Products, Inc. Birmingham, AL
Natural rubber	Edmont Coshocton, OH	26-680	21	Southern Safety Products, Inc. Birmingham, AL
Nitrile rubber	Edmont Coshocton, OH	37-165	22	Southern Safety Products, Inc. Birmingham, AL

TABLE 2. AVERAGE SOLUBILITIES AND DIFFUSION COEFFICIENTS CALCULATED FROM LIQUID-IMMERSION ABSORPTION AND DESORPTION TEST DATA

Glove	Solvent	Solubility, g/cm³	Diffusion coefficient,[a,b,c] cm²/sec			
			$10^9 \times D_a$	$10^9 \times D_d$	$10^9 \times D'_a$	$10^9 \times D'_d$
Butyl rubber	Acetone	0.0457 ± 0.0010	5.6 ± 1.4	--	5.0 ± 0.79	--
	Cyclohexane	2.7261 ± 0.1088	150 ± 3.4	330 ± 7.3	180 ± 19	280 ± 82
	Isopropanol	0.0041 ± 0.0010	7.1 ± 13	--	0.43 ± 0.23	--
	Toluene	1.7690 ± 0.0372	380 ± 13	280 ± 120	320 ± 110	210 ± 110
Natural rubber	Acetone	0.1527 ± 0.0099	400 ± 200	380 ± 20	690 ± 230	450 ± 55
	Cyclohexane	2.6877 ± 0.0635	250 ± 30	490 ± 150	260 ± 12	480 ± 150
	Isopropanol	0.0489 ± 0.0019	42 ± 6.4	--	40 ± 20	--
	Toluene	3.2067 ± 0.1524	530 ± 61	260 ± 35	580 ± 51	290 ± 25
Neopren rubber	Acetone	0.4044 ± 0.0262	250 ± 200	260 ± 36	520 ± 64	311 ± 50
	Cyclohexane	0.8781 ± 0.0139	37 ± 6.1	54 ± 4.4	40 ± 2.3	43 ± 6.5
	Isopropanol	0.0574 ± 0.0079	1.3 ± 0.67	--	1.2 ± 0.31	--
	Toluene	3.1388 ± 0.0914	350 ± 38	200 ± 33	410 ± 7.8	210 ± 46
Nitrile rubber	Acetone	1.8204 ± 0.1236	420 ± 59	450 ± 82	440 ± 160	480 ± 61
	Cyclohexane[d]	0.0982 ± 0.0195	0.25 ± 0.067	--	0.30 ± 0.080	--
	Isopropanol[d]	0.2340 ± 0.0234	0.42 ± 0.20	--	0.72 ± 0.23	--
	Toluene	1.4377 ± 0.0463	59 ± 5.9	200 ± 40	98 ± 15	150 ± 18

[a]The term D_a is the apparent diffusion coefficient estimated from the initial slope of the reduced absorption curve. D_d is the apparent diffusion coefficient estimated from the initial slope of the reduced desorption curve. All data points [including (0,0)] for which $M_t/M_\infty < 0.6$ were used in these calculations; if no data points meeting this criterion except (0,0) existed, then the calculation was based on (0,0) and the first data point above $M_t/M_\infty = 0.6$.

[b]The term D'_a is the apparent diffusion coefficient calculated from a curve-fit of data obtained in an absorption test.
D'_d is the apparent diffusion coefficient calculated from a curve-fit of data obtained in a desorption test.

[c]The symbol "--" means that the experiment indicated was not conducted.

[d]Some of the nitrile-rubber samples immersed in these solvents continued to gain weight even after 530 hr.

TABLE 3. COMPARISON OF MEASURED BREAKTHROUGH TIMES AND STEADY-STATE PERMEATION RATES WITH THOSE PREDICTED FROM IMMERSION TEST DATA[a]

Glove	Solvent	Breakthrough time,[b] min		Steady-state permeation rate, μg/(cm²·min)	
		Measured	Predicted	Measured	Predicted
Butyl rubber	Acetone	>1100	∞	<0.47	0.25 ± 0.05
	Cyclohexane	55 ± 6.3	5.5 ± 0.4	440 ± 110	660 ± 53
	Isopropanol	--	∞	--	0.028 ± 0.05
	Toluene	24	4.7 ± 0.5	400	560 ± 91
Natural rubber	Acetone	17 ± 1.2	9.9 ± 5.3	36 ± 3.5	51 ± 22
	Cyclohexane	19 ± 1.7	4.7 ± 0.8	520 ± 48	900 ± 160
	Isopropanol	>150, <1400	130 ± 35	1	2.2 ± 0.7
	Toluene	9.7 ± 1.5	4.0 ± 0.1	780 ± 27	1200 ± 2.5
Neoprene rubber	Acetone	22 ± 2.0	8.6 ± 0.0	150 ± 20	120 ± 68
	Cyclohexane	>60	28 ± 3.8	35 ± 27	49 ± 5.5
	Isopropanol	--	∞	--	0.10 ± 0.05
	Toluene	12	3.2 ± 0.2	640	1100 ± 45
Nitrile rubber	Acetone	10 ± 2.0	3.2 ± 0.2	960 ± 26	810 ± 81
	Cyclohexane	>1400	∞	<0.12	0.028 ± 0.01
	Isopropanol	--	∞	--	0.11 ± 0.06
	Toluene	52	12 ± 1.4	210	190 ± 19

[a]The symbol "--" means that no permeation test was conducted with this glove/solvent combination. The symbol "∞" means that the permeation rate would always be less than that used to define the breakthrough time.

[b]The predicted breakthrough times are based on the minimum permeation rates that could be detected in permeation tests: 0.47 μg/(cm²·min) for acetone, 0.12 μg/(cm²·min) for cyclohexane, and 0.11 μg/(cm²·min) for toluene, and 0.31 μg/(cm²·min) for isopropanol.

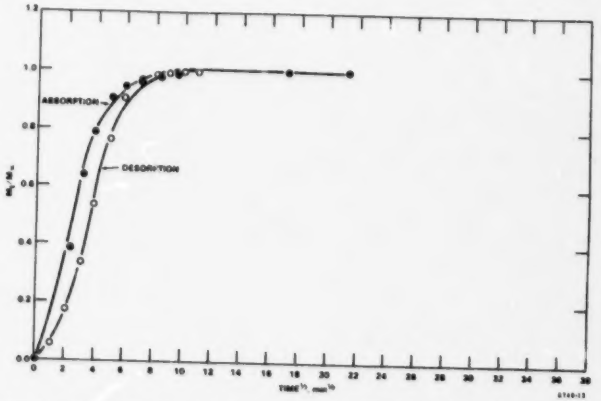

Figure 1. Absorption and desorption curves for toluene in natural rubber.

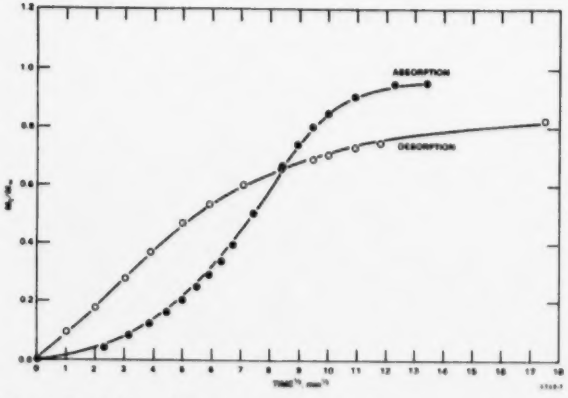

Figure 2. Adsorption and desorption curves for cyclohexane in neoprene rubber.

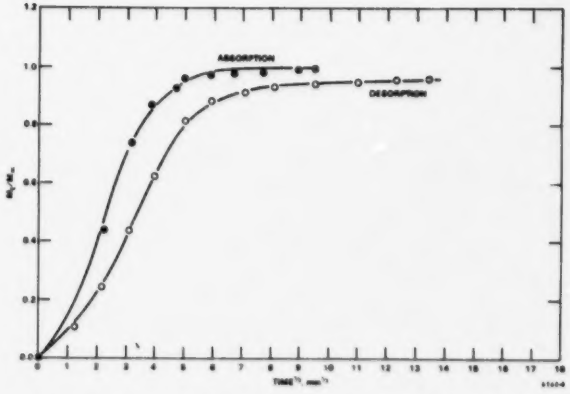

Figure 3. Absorption and desorption curves for toluene in neoprene rubber.

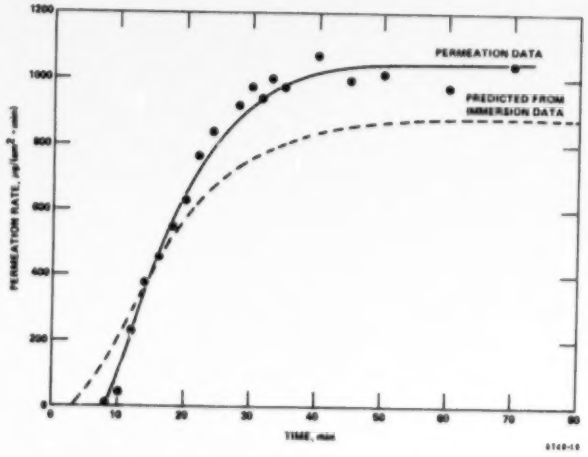

Figure 4. Comparison of predicted and experimental permeation-rate curves for acetone through nitrile rubber.

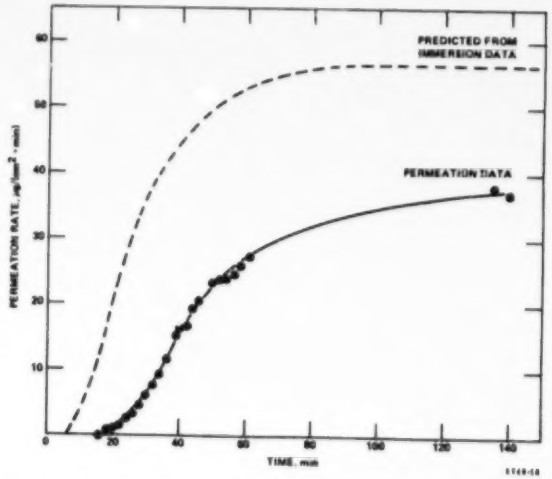

Figure 5. Comparison of predicted and experimental permeation-rate curves for acetone through natural rubber.